J. Am. Chem. Soc. **1981**, *103*, 7796–7797

Spectroscopic Properties and Redox Chemistry of the Phosphorescent Excited State of $Pt_2(P_2O_5)_4H_8^{4-}$

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Binuclear complexes built from square-planar Rh(I) or Ir(I) isocyanide units exhibit rich photophysical and photochemical properties.[1-9] Extensive studies in our laboratory have established that the lowest electronic excited states of one of these complexes, $Rh_2b_4^{2+}$ (b = 1,3-diisocyanopropane) [$^1A_{1g}$ (D_{4h}) ground state; Rh–Rh = 3.24 Å),[10,11] are a spin triplet ($^3A_{2u}$) and a spin singlet ($^1A_{2u}$) derived from the $d\sigma^*p\sigma(1a_{2u}2a_{1g})$ orbital configuration[5,8] and that the $E_u(^3A_{2u})$ phosphorescent state ($\tau = 8.5$ μs, CH_3CN solution, 25 °C)[8] undergoes electron-transfer reactions with donors and acceptors.[4] Our decision to begin experiments with the goal of extending this type of photochemistry to analogous Pt(II) complexes was based mainly on reports of an intensely luminescent, phosphite-bridged binuclear species, $Pt_2(P_2O_5)_4H_8^{4-}$ (Pt–Pt = 2.93 Å).[12-14] Our experiments have shown that the properties of the lowest electronic excited states of $Pt_2(P_2O_5)_4H_8^{4-}$ are entirely analogous to those of $Rh_2b_4^{2+}$, and they have provided the first examples of electron-transfer reactions involving excited Pt(II) species and acceptor molecules.

The electronic absorption spectrum of an aqueous solution of $K_4[Pt_2(P_2O_5)_4H_8]$ exhibits bands at 367 (ϵ_{max} 3.45×10^4) and 452 nm (ϵ 1.1×10^2 mol^{-1} dm^3 cm^{-1}) (Figure 1).[15] The intense 367-nm band is attributable to the $^1A_{2u} \leftarrow {}^1A_{1g}$ transition, whereas the band at 452 nm is due to the $^3A_{2u} \leftarrow {}^1A_{1g}$ transition.[16] Excitation (367 nm) of a degassed aqueous solution of $K_4[Pt_2(P_2O_5)_4H_8]$ at room temperature results in fluorescence (λ_{max} = 407 nm, $\tau < 2$ ns; $^1A_{2u} \rightarrow {}^1A_{1g}$) and phosphorescence ($\lambda_{max}$ = 517 nm, τ = 9.8 (2) μs; $^3A_{2u} \rightarrow {}^1A_{1g}$).[17,18] The same sample phosphoresces at 517 nm upon excitation at 452 nm. Addition of O_2 results in significant quenching of the phosphorescence (τ = 0.9 (1) μs; $[Pt_2(P_2O_5)_4H_8^{4-}] \sim 10^{-4}$–$10^{-5}$ M, O_2 saturated), but such addition has no appreciable effect on the intensity of the fluorescence.

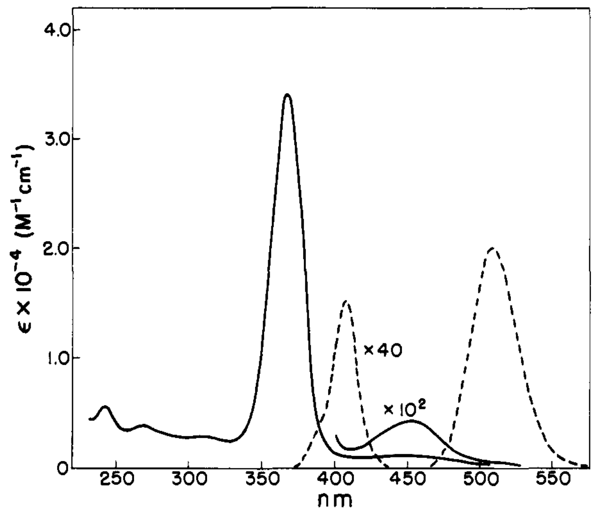

Figure 1. Absorption (—; left scale for ϵ values) and corrected emission (- - -) spectra of an aqueous solution (25 °C) of $K_4[Pt_2(P_2O_5)_4H_8]$.

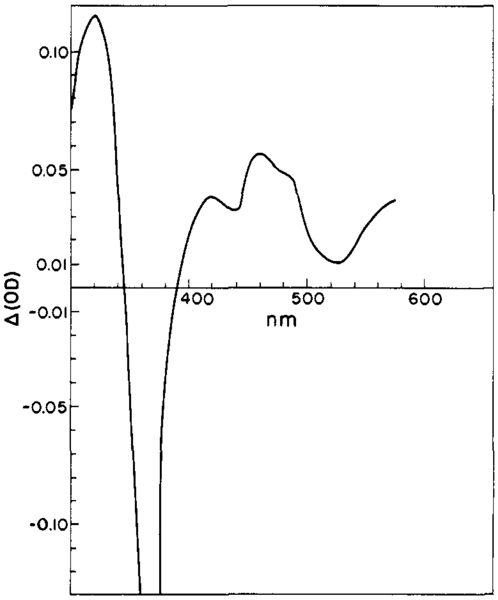

Figure 2. Transient difference spectrum of a degassed aqueous solution (25 °C) of $K_4[Pt_2(P_2O_5)_4H_8]$; the experiment employed Nd:YAG laser (fwhm, 8 ns) excitation (third harmonic, 355 nm).

The transient difference spectrum of a degassed aqueous solution of $Pt_2(P_2O_5)_4H_8^{4-}$ upon 355-nm excitation is shown in Figure 2. The decay of the transient is first order at all wavelengths (τ = 11 (1), 460; 10 (1) μs, 380 nm), and the transient spectrum shows bleaching of the ground-state absorption between 330 and 400 nm. The results show that the transient is the phosphorescent state, $^3A_{2u}$. The intense absorption band at 325 nm in the $^3A_{2u}$ spectrum unquestionably is an allowed transition, and one reasonable assignment is $d\sigma \rightarrow d\sigma^*$.

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(15) Microcrystalline $K_4[Pt_2(P_2O_5)_4H_8]$ was prepared by a modified version of a literature procedure.[13] K_2PtCl_4 (0.8 g) and phosphorous acid (2.8 g) in 5 mL of water were heated in a steam bath for 2 h. The resulting solution was then evaporated to dryness in an oven at 110 °C, and a light greenish solid was obtained. The solid was washed with methanol and acetone to remove the unreacted phosphorous acid, and the resulting material was dissolved in about 10 mL of water. After the solution was filtered, methanol or acetone was added slowly to the filtrate, producing microcrystalline $K_4[Pt_2(P_2O_5)_4H_8]$.

(16) Spectroscopic studies on single crystals of $K_4[Pt_2(P_2O_5)_4H_8]$ have been performed (Che, C.-M.; Rice, S. F., unpublished results). The 367-nm band is polarized parallel to the Pt–Pt axis, and the 452-nm system (466 nm in the crystal spectrum) is perpendicularly polarized. Thus the 452-nm band is $E_u(^3A_{2u}) \rightarrow {}^1A_{1g}$.

(17) Similar emission spectra also were observed for microcrystalline samples of $K_4[Pt_2(P_2O_5)_4H_8]$ and $[Ph_4As]_4[Pt_2(P_2O_5)_4H_8]$. The phosphorescence lifetime of the solid potassium salt at room temperature is 3.7 μs (λ_{max} = 509 nm), and at 77 K it is 7.1 μs. $[Ph_4As]_4[Pt_2(P_2O_5)_4H_8]$ was prepared by metathesis of $[Ph_4As]Cl$ and $K_4[Pt_2(P_2O_5)_4H_8]$ in aqueous solution.

(18) Where there is overlap, our results accord with those of Fordyce, Bremmer, and Crosby, who have studied the emission properties of $K_4[Pt_2(P_2O_5)_4H_8]$ over a wide temperature range.[4]

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The phosphorescence of in aqueous solution is quenched by 1,1′-bis(2-sulfoethyl)-4,4′-bipyridinium inner salt (BSEP). Transient absorption attributable to BSEP$^-$ ($\lambda_{max} \sim 610$ nm)[19] is observed in flash kinetic spectroscopic studies of aqueous solutions containing $\mathrm{Pt_2(P_2O_5)_4H_8^{4-}}$ and BSEP, thereby establishing an electron-transfer quenching mechanism:

$$\mathrm{Pt_2(P_2O_5)_4H_8^{4-} + BSEP \xrightarrow{k_q} Pt_2(P_2O_5)_4H_8^{3-} + BSEP^-}$$

Stern–Volmer analysis of the quenching yields $k_q = 5.5 \times 10^9$ M^{-1} s^{-1} ($[\mathrm{Pt_2(P_2O_5)_4H_8^{4-}}] \sim 10^{-4}$ M; 0.1 M $\mathrm{NaClO_4}$; 25 °C). Both the quenching reaction and the bimolecular back-electron-transfer ($k = 1 \times 10^9$ M^{-1} s^{-1} for $\mathrm{Pt_2(P_2O_5)_4H_8^{3-}}$ and BSEP$^-$) are near the diffusion limit for such processes in aqueous solution at 25 °C.

The $^3A_{2u}(d\sigma^*p\sigma)$ state of $\mathrm{Pt_2(P_2O_5)_4H_8^{4-}}$ is an extremely powerful one-electron reductant in aqueous solution. Preliminary experiments have shown that species such as $\mathrm{Os(NH_3)_5Cl^{2+}}$ ($E_{1/2} = -1.09$ V vs. SCE)[20] and nicotinamide ($E_{1/2} = -1.44$ V vs. Ag/AgCl; $\mathrm{CH_3OH}$, pH 7.2)[21] are readily reduced by $\mathrm{Pt_2(P_2O_5)_4H_8^{4-*}}$. From these and related experiments it is apparent that $\mathrm{Pt_2(P_2O_5)_4H_8^{4-*}}$ is a stronger reducing agent [$E°(3-/4-*) < -1$ V vs. NHE][22] than $\mathrm{Ru(bpy)_3^{2+*}}$ ($E° = -0.88$ V vs. NHE)[23] in aqueous solution. We are now exploring several aspects of the photoredox chemistry of $\mathrm{Pt_2(P_2O_5)_4H_8^{4-}}$, as the ease of generation of $\mathrm{Pt_2(P_2O_5)_4H_8^{4-*}}$ suggests that it will be a useful reagent for a variety of substrate reductions.

Acknowledgment. We thank D. S. Kliger and R. A. Goldbeck for assistance with some of the laser flash spectroscopic experiments. We are indebted to A. W. Maverick, S. J. Milder, V. M. Miskowski, D. G. Nocera, and S. F. Rice for several helpful discussions. This research was supported by National Science Foundation Grant CHE78-10530.

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[22] It has not been possible to obtain a better estimate of $E°(4-*/3-)$ from spectroscopic and electrochemical measurements, because the electrochemical oxidation of $\mathrm{Pt_2(P_2O_5)_4H_8^{4-}}$ in aqueous solution at 25 °C is not reversible (cyclic voltammetric measurements; graphite electrode; scan speed, 500 mV/s; $\mathrm{K_4[Pt_2(P_2O_5)_4H_8]}$, 0.1 M $\mathrm{NaClO_4}$).

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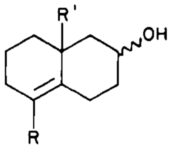
Additions and Corrections

On the Nonconcertedness of Allylic Cation Promoted π-Cyclization Reactions [*J. Am. Chem. Soc.* **1981**, *103*, 1285]. MLADEN LADIKA, IVO BREGOVEC, and DIONIS E. SUNKO,* Department of Chemistry, Faculty of National Sciences and Mathematics, University of Zagreb, 41000 Zagreb, Yugoslavia.

Page 1286: Structures **7** and **8** should be:



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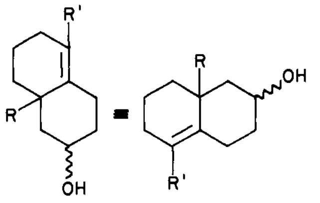

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Stereochemical Analysis of γ-Replacement and γ-Elimination Processes Catalyzed by a Pyridoxal Phosphate Dependent Enzyme [*J. Am. Chem. Soc.* **1981**, *103*, 4921]. MICHAEL N. T. CHANG and CHRISTOPHER T. WALSH,* Departments of Chemistry and Biology, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Page 4925, Scheme VII: The last species is 4-*S*-2-ketobutyrate, not 4*R* as written.

Page 4925, 5th and 6th lines from the bottom, first column: The text should read "conversion of (*Z*)- and (*E*)-[4-^{2}H]-vinylglycines to (4*S*)- and (4*R*)-[^{1}H,^{2}H,^{3}H]-2-ketobutyrates, respectively, can be interpreted." The *S* and *R* designations were inadvertently transposed.

Page 4923, Table II, line 3: The numbers 1027.5 and 1029.3 are incorrectly transposed. The (*E*)-[4-^{2}H]-vinylglycine yields the 1029.3 sample of homoserine, the (*Z*)-vinylglycine yields the 1027.5 sample.

Synthesis, Structure, and Stability of (i,o)-Bicyclo[6.2.2]dodeca-9,11-dienes. Generation of Unusually Expanded Carbon–Carbon–Carbon Bond Angles [*J. Am. Chem. Soc.* **1981**, *103*, 215]. PAUL G. GASSMAN* and REBECCA C. HOYE, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

Page 217: In Table II for atom O2, the *z* value should be 0.4691 (1) instead of 0.4961 (1).

α-Disulfoxide and Sulfinic Anhydride in the Peroxy Acid Oxidation of 2-Methyl-2-propyl 2-Methyl-2-propanethiosulfinate [*J. Am. Chem. Soc.* **1981**, *103*, 6232–6235]. FILLMORE FREEMAN* and CHRISTOS N. ANGELETAKIS, Department of Chemistry, University of California, Irvine, California 92717.

Authors should read: Fillmore Freeman* and Christos N. Angeletakis, Department of Chemistry, University of California, Irvine, California 92717, and Tom J. Maricich, Department of Chemistry, California State University, Long Beach, California 90840.